Supporting Information

for

PNP complexes in the sp^3 C-H bond activation of methyl propanoate and related esters

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O CONTENTS

O SECTION S-1: CRYSTALLOGRAPHIC DISCUSSION

Single crystals of **2**, suitable for structure determination by X-ray diffraction, were grown by slow diffusion of hexane into a solution of **2** in dichloromethane at room temperature. Complex **2** crystallises as yellow prisms in the triclinic space group *P*ī with the asymmetric unit consisting of one molecule of **2** together and one dichloromethane molecule. The collected data set was of sufficient quality to allow for the location of the hydride atom. The hydrogen atoms for the water molecule and the hydride were located from a difference Fourier map. Those hydrogen atoms were refined subject to distance restraints with the hydride hydrogen atom being refined isotropically and the water hydrogen atoms using a riding model. An ellipsoid representation of the molecular structure is displayed in Figure S1 with selected bond lengths and angles summarised in Table S1. Analysis of the determined structure reveals a distorted octahedral geometry about the central Ir(III) atom with the propanoate coordinated in the equatorial plane *trans* to nitrogen with the hydride and water ligands occupying mutually *trans* axial positions. A hydrogen bond exists between the carbonyl oxygen and the coordinated water molecule, forming a six membered ring which aids in stabilising the structure. Within the structure of **2**, the pyridine ring, Ir(III) centre and coordinated propanoate oxygen atom all lie essentially within the same plane. Both P-atoms, however, lie slightly above the plane at torsion angles of 1.4(4)° and 8.7(4)°, pointing away from the coordinated propanoate ligand in order to minimise steric congestion [Figure S2 (b)]. As a consequence of this twisting, the P(1)–Ir(1)–P(2) angle deviates significantly from linearity, with the measured P(1)–Ir(1)–O(2) and P(2)–Ir(1)–O(2) angles widened to give angles greater than the ideal 90°. The measured Ir(1)–O(28) [2.283(6) Å] and Ir(1)–H(1) [1.65(2) Å] bond lengths are comparable to those of the C–H activated acetone complex [Ir(PNP)(H)(H_2O){$CH_2C(O)CH_3$}][BF_4] reported in the literature [2.288(4) Å and 1.50(7) Å, respectively].[1] A significantly shorter Ir(1)–N(1) [2.068(7) Å] separation is, however, observed for **2** when compared to that of the mentioned literature example [2.136(4) Å], owing to the weaker *trans* influence of the propanoate O-atom compared to that of the methylene group coordinated *trans* to nitrogen in [Ir(PNP)(H)(H_2O){$CH_2C(O)CH_3$}][BF_4].[1]

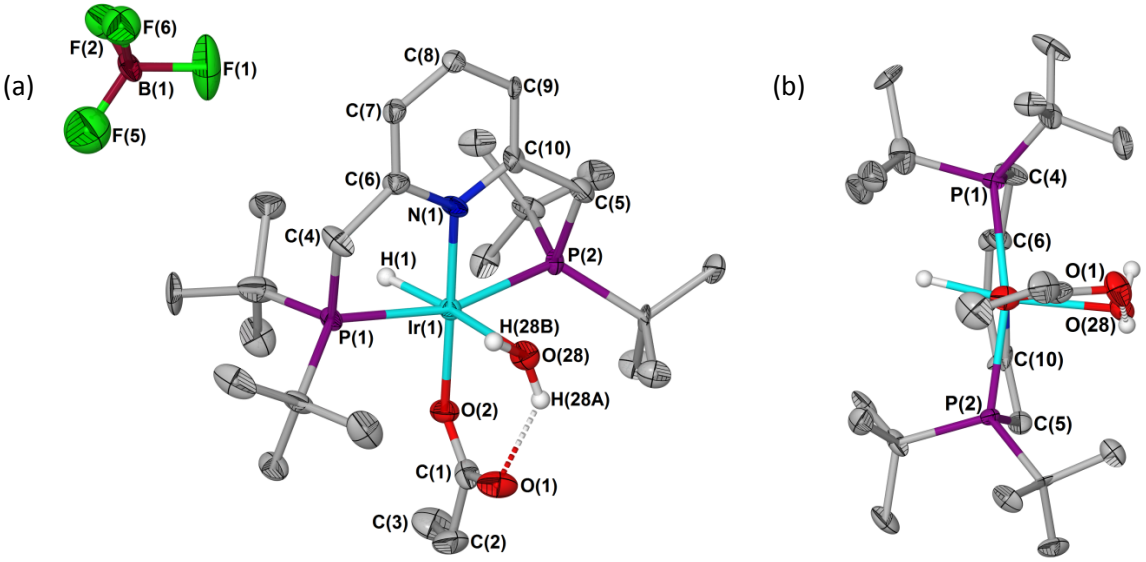

Figure S1 a) Molecular structure of **2** showing the numbering scheme. Thermal ellipsoids set at 50 % probability and hydrogen atoms (with the exception of the hydride and water protons), BF_4 counterion and solvent molecule are omitted for clarity; (b) side view of the structure (BF_4 omitted for clarity).

Table S1 Selected bond lengths (Å) and angles (°) of **2** with estimated standard deviations in parenthesis.

Bond lengths (Å)

Ir(1)–P(1)	2.323(2)	Ir(1)–H(1)	1.65(2)
Ir(1)–P(2)	2.347(2)	C(1)–O(1)	1.230(11)
Ir(1)–N(1)	2.068(7)	C(1)–O(2)	1.276(11)
Ir(1)–O(2)	2.085(6)	C(1)–C(2)	1.530(13)
Ir(1)–O(28)	2.283(6)	C(2)–C(3)	1.494(14)

Bond angles (°)

P(1)–Ir(1)–P(2)	161.94(8)	C(5)–P(2)–Ir(1)	96.7(3)
P(1)–Ir(1)–N(1)	84.3(2)	C(4)–C(6)–N(1)	117.2(8)
P(1)–Ir(1)–O(2)	95.39(18)	C(5)–C(10)–N(1)	117.6(7)
P(1)–Ir (1)–O(28)	101.05(17)	O(2)–Ir(1)–O(28)	94.5(2)
P(1)–Ir(1)–H(1)	70(3)	O(2)–Ir(1)–N(1)	179.0(3)
P(2)–Ir(1)–N(1)	84.4(2)	O(2)–Ir(1)–H(1)	87(3)
P(2)–Ir(1)–O(2)	95.73(18)	O(28)–Ir(1)–N(1)	86.5(3)
P(2)–Ir(1)–O(28)	92.22(16)	O(28)–Ir(1)–H(1)	171(3)
P(2)–Ir(1)–H(1)	96(3)	N(1)–Ir(1)–H(1)	92(3)
P(1)–C(4)–C(6)	113.3(6)	O(1)–C(1)–O(2)	126.4(8)
P(2)–C(5)–C(10)	112.2(5)	O(2)–C(1)–C(2)	114.1(7)
C(4)–P(1)–Ir(1)	98.9(3)	O(1)–C(1)–C(2)	119.4(8)

The structure of **3** could also be confirmed crystallographically and crystals suitable for crystal and molecular structure determinations were grown by slow diffusion of pentane into a dichloromethane solution of **3**. An ellipsoid representation of the molecular structure of **3** is depicted in Figure S2, while selected bond lengths and angles are listed in Table S1. Complex **3** crystallises as orange plates in the monoclinic spacegroup $P2_1/n$ with Z = 4 molecule in the asymmetric unit. Although the relatively low electron density of the hydridic hydrogen atoms did not allow for their placement, the presence of these atoms could be confirmed by ^{1}H NMR spectroscopic analysis of the isolated crystals. The carbonyl group is located in the plane of the PNP ligand ring, and the hydride ligands can therefore be assumed to occupy positions *trans* to one another with the molecule adopting an overall distorted octahedral geometry about the central Ir(III) atom. As a rule, such *trans*-dihydride complexes are not normally favoured over their *cis* counterparts, owing to the destabilising influence of having two strongly sigma donating ligands in mutually *trans* positions.[2] However, despite this destabilising influence, *trans* dihydrido iridium pincer complexes are not uncommon and a number of such complexes, including the analogous *trans*-[Ir(CO)(H)$_2$(PNP)][PF$_6$], have been reported in literature.[2-7] Moreover, the *trans* isomer has even be shown by Rybtchinski and co-workers[5] to be thermodynamically favoured over the *cis* isomer in the case of [Ir(CO)(H)$_2$(PCP)] [where PCP = 1,3-bis{(diisopropylphosphino)methyl}phenyl]. While the CO ligand, Ir centre, pyridine ring and methylene groups of **3** all lie approximately within the same plane, the two phosphorus atoms are twisted with respect to the plane at torsion angles of 13.3(4)^o [P(1)–Ir(1)–N(1)–C(4)] and 9.6(4)^o [P(2)–Ir(1)–N(1)–C(8)] with one P-atom above and one below the plane [Figure 5.2 (b)]. All bond lengths and angles are in good agreements with the PF$_6$ analogue, *trans*–[Ir(CO)(H)$_2$(PNP)][PF$_6$], reported in the literature.[2]

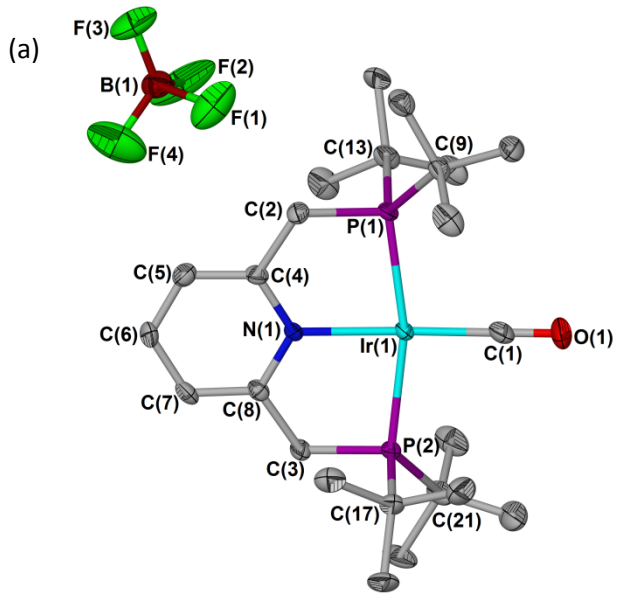

Figure S1 (a) Molecular structure of the dihydrido CO complex **3** showing the numbering scheme. Thermal ellipsoids set at 50 % probability and hydrogen atoms are omitted for clarity. Hydride atoms are not located owing to their low relative electron densities; (b) Side view of the molecular structure of **3** (BF_4 omitted for clarity).

Table S1 Selected bond lengths (Å) and angles (°) of **3** with estimated standard deviations in parenthesis.

Bond lengths (Å)

Ir(1)–P(1)	2.3270(18)	Ir(1)–C(1)	1.864(8)
Ir(1)–P(2)	2.3242(19)	C(1)–O(1)	1.144(11)
Ir(1)–N(1)	2.119(6)		

Bond angles (°)

P(1)–Ir(1)–P(2)	165.95(7)	P(2)–C(3)–C(8)	112.8(5)
P(1)–Ir(1)–N(1)	82.80(15)	C(2)–P(1)–Ir(1)	98.9(2)
P(1)–Ir(1)–C(1)	98.1(3)	C(3)–P(2)–Ir(1)	98.7(2)
P(2)–Ir(1)–N(1)	83.18(15)	C(2)–C(4)–N(1)	117.5(6)
P(2)–Ir(1)–C(1)	95.9(3)	C(3)–C(8)–N(1)	117.6(6)
N(1)–Ir(1)–C(1)	176.6(3)	Ir(1)–C(1)–O(1)	179.0(8)
P(1)–C(2)–C(4)	112.3(5)		

SECTION S-2: CRYSTALLOGRAPHIC DATA TABLE

Table S3 Crystallographic data for compounds **2** and **3**.*

Compound reference	**2**	**3**
Empirical formula	$C_{27}H_{53}BCl_2F_4IrNO_3P_2$	$C_{24}H_{43}BF_4IrNOP_2$
Formula weight (g/mol)	851.60	702.58
Temp. (K)	93(2)	93(2)
Wavelength (Å)	0.71075	0.71075
Crystal system	Triclinic	Monoclinic
Crystal dimensions (mm^3)	0.15 × 0.15 × 0.10	0.38 × 0.34 × 0.04
Crystal shape and colour	Prism, yellow	Prism, yellow
Space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a (Å)	9.2649(16)	12.306(2)
b (Å)	10.9156(19)	8.3002(15)
c (Å)	17.297(3)	28.365 (5)
α (°)	85.604(11)	90.00
β (°)	84.512(11)	92.010(5)
γ (°)	79.863(9)	90.00
Unit cell volume ($Å^3$)	1710.9(5)	2895.5(9)
No. of formula units per unit cell, Z	2	4
d_{calcd} (g/cm^3)	1.653	1.612
Radiation type	MoKα	MoKα
Absorption coefficient, μ (mm^{-1})	4.213	4.777
F(000)	856	1400
θ-range for data collection (°)	2.45 to 25.35	2.55 to 30.08
Index range	-10 ≤ h ≤ 11, -8 ≤ k ≤ 13, -18 ≤ l ≤ 20	0 ≤ h ≤ 17, -11 ≤ k ≤ 11, -40 ≤ l ≤ 40
No. of reflections measured	10841	15439
No. of independent reflections	6025	5147
Refinement parameters / restraints	413 / 2	319 / 0
R_{int}	0.0544	0.0705
Final R_1 values ($I > 2\sigma(I)$)	0.0563	0.0485
Final R_1 values (all data)	0.0666	0.0525
Final $wR(F^2)$ values (all data)	0.1544	0.1247
Goodness of fit on F^2	1.078	1.087
Largest diff. peak and hole ($e.A^{-3}$)	1.86 to -2.20	1.78 to -1.62
Weighing scheme †	a = 0.0729 b = 3.3405	a = 0.0491 b = 16.7504

* The full Crystallographic Information Framework (CIF) files are available as supplementary information.

† $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(aP)^2+bP+d+\sin\theta]$; $P = [f(\text{Max}(0 \text{ or } F_o^2)] + (1\text{-}f)\ F_c^2$

SECTION S-3: NMR SPECTRA

^{1}H NMR spectrum of **2**.

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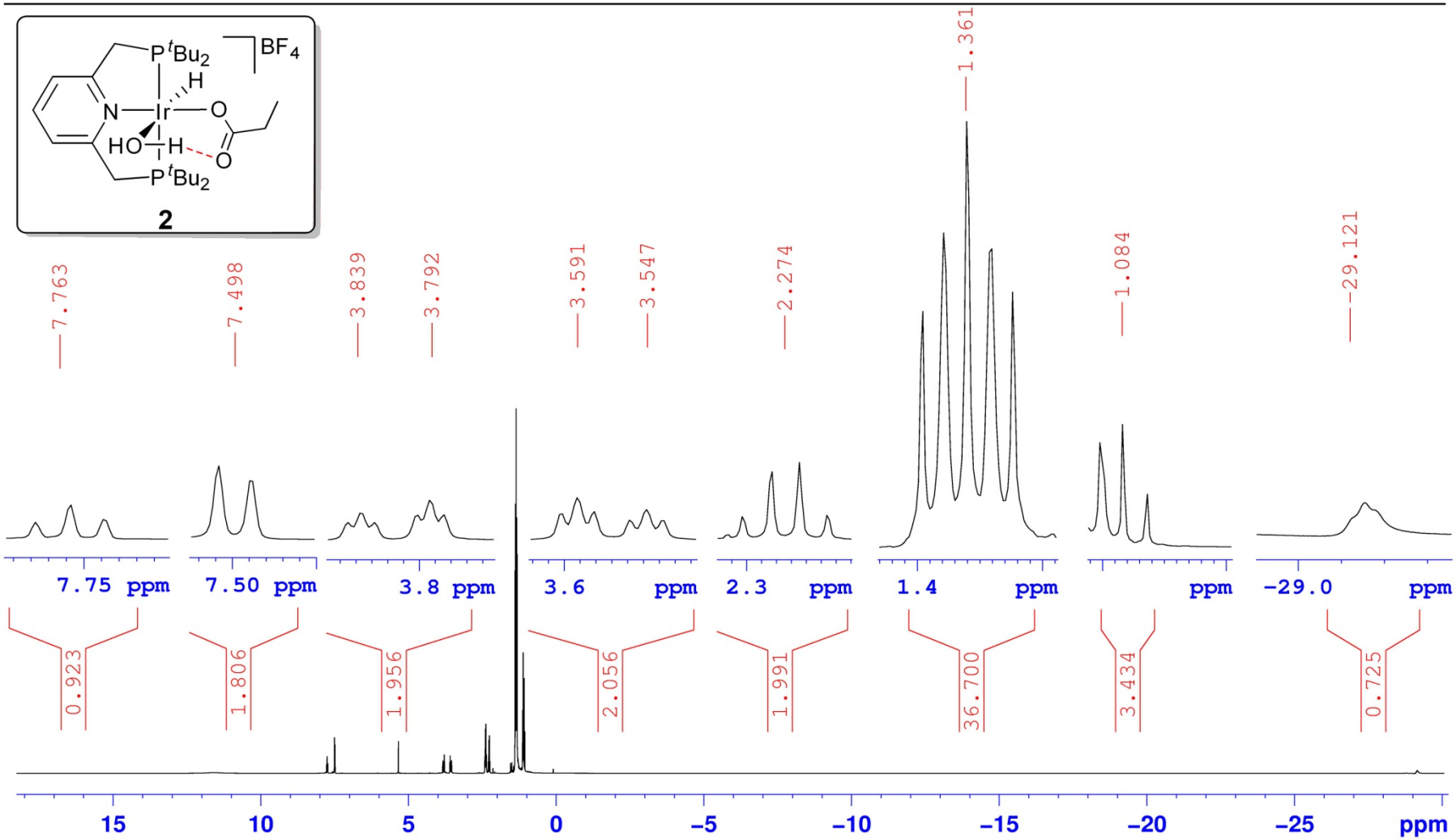

$^{13}C\{^{1}H\}$ DEPT NMR spectrum of **2**.

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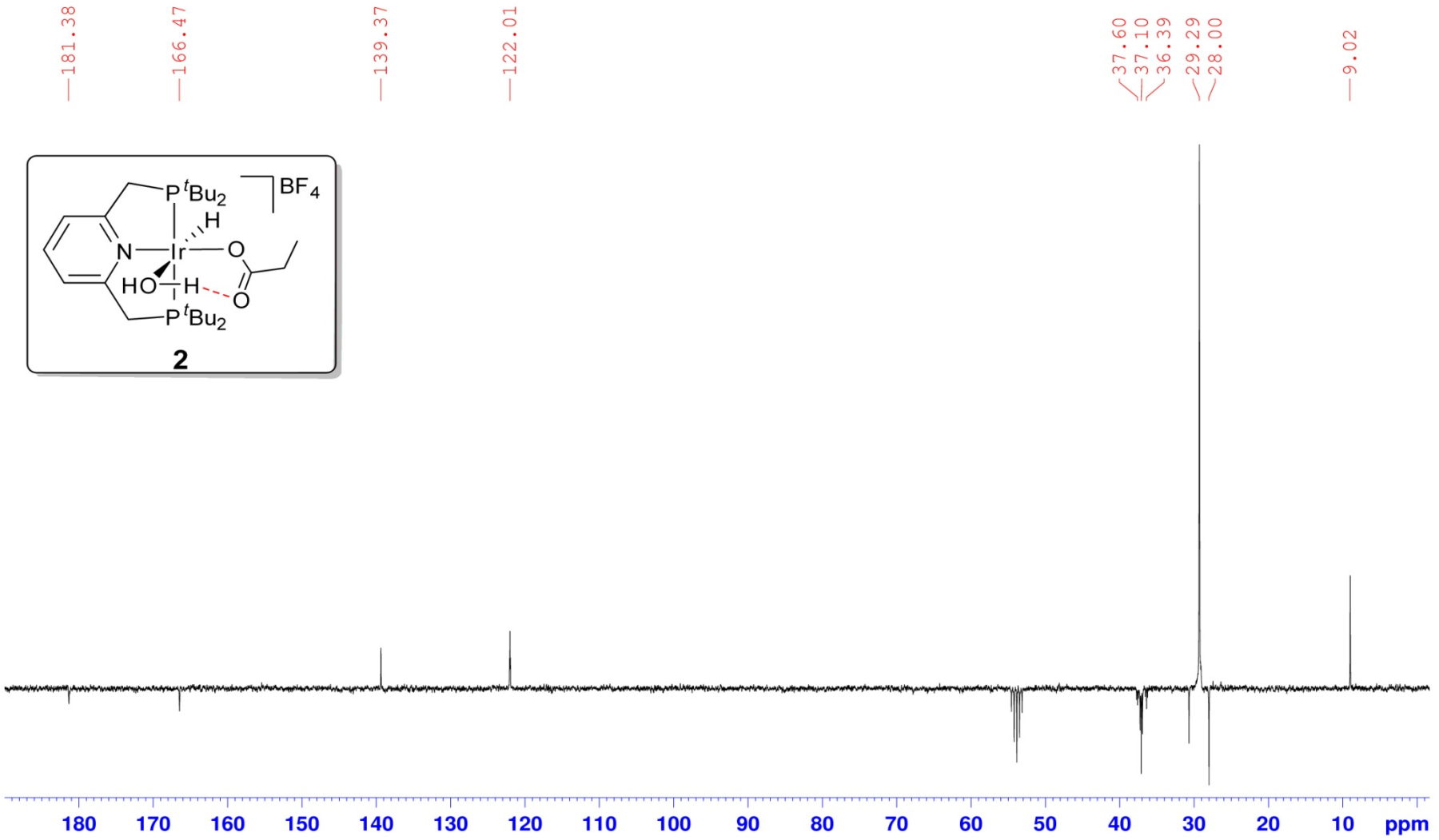
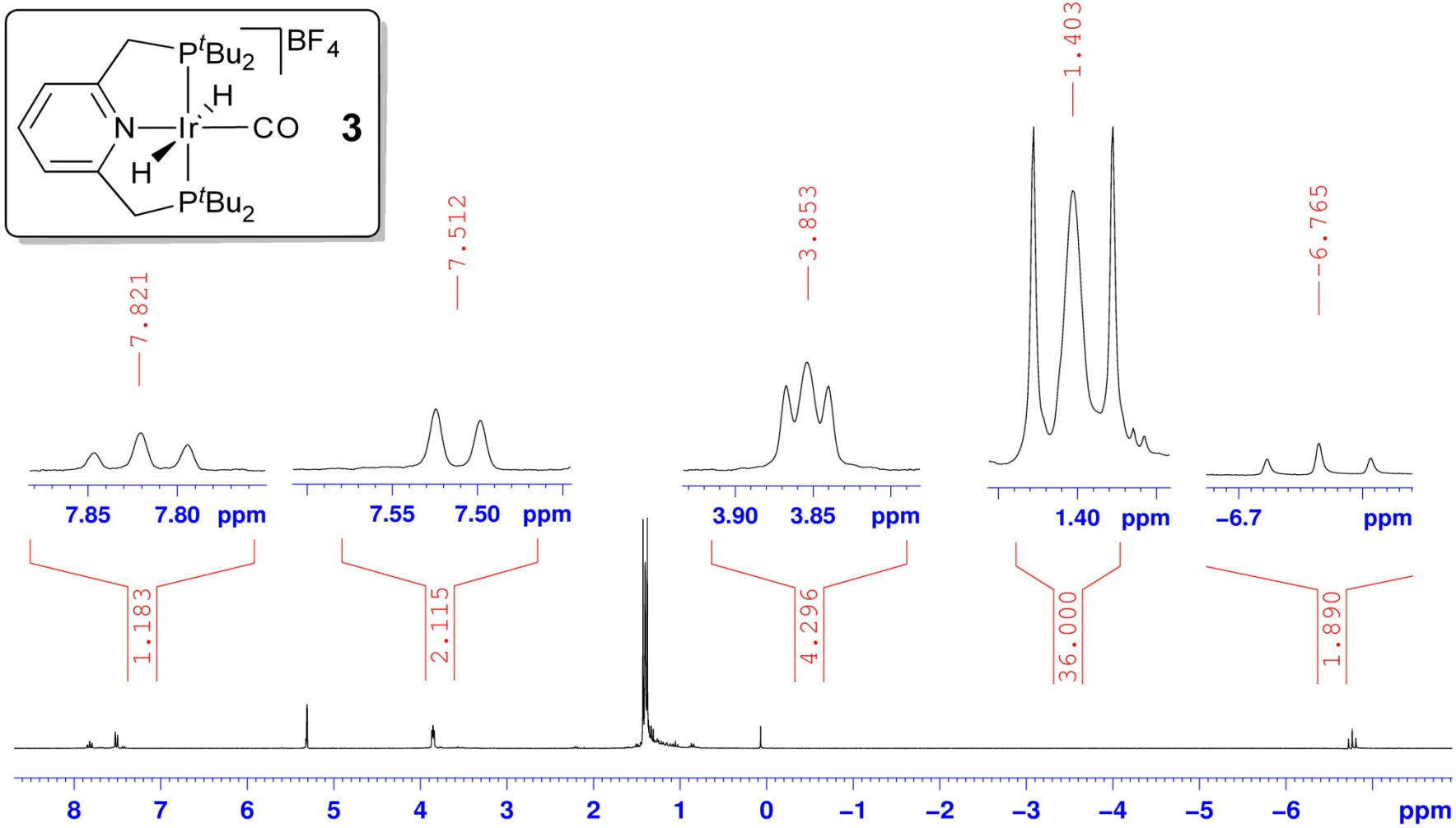


^{1}H NMR spectrum of **3**.



^{1}H NMR spectrum of **6**.

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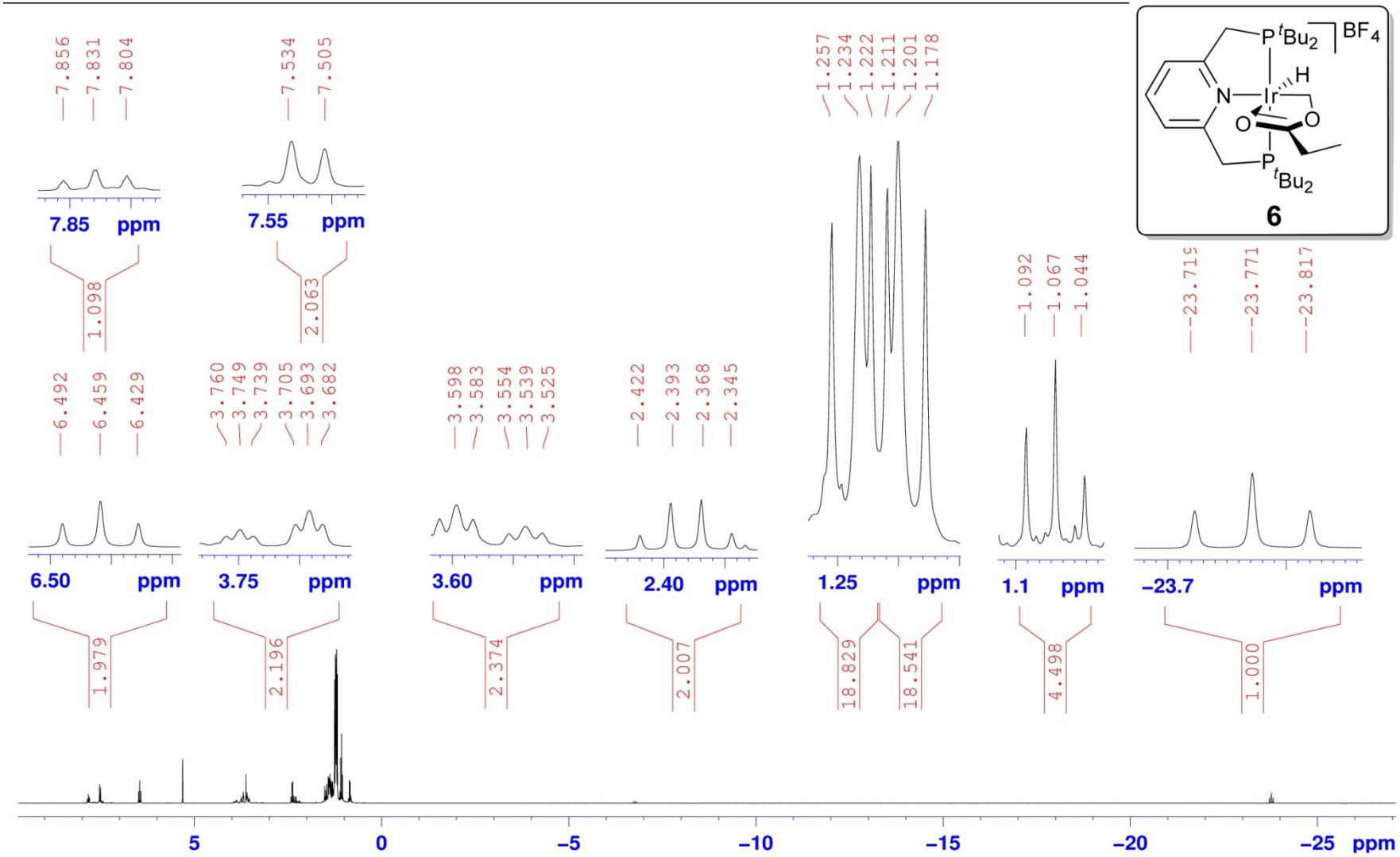

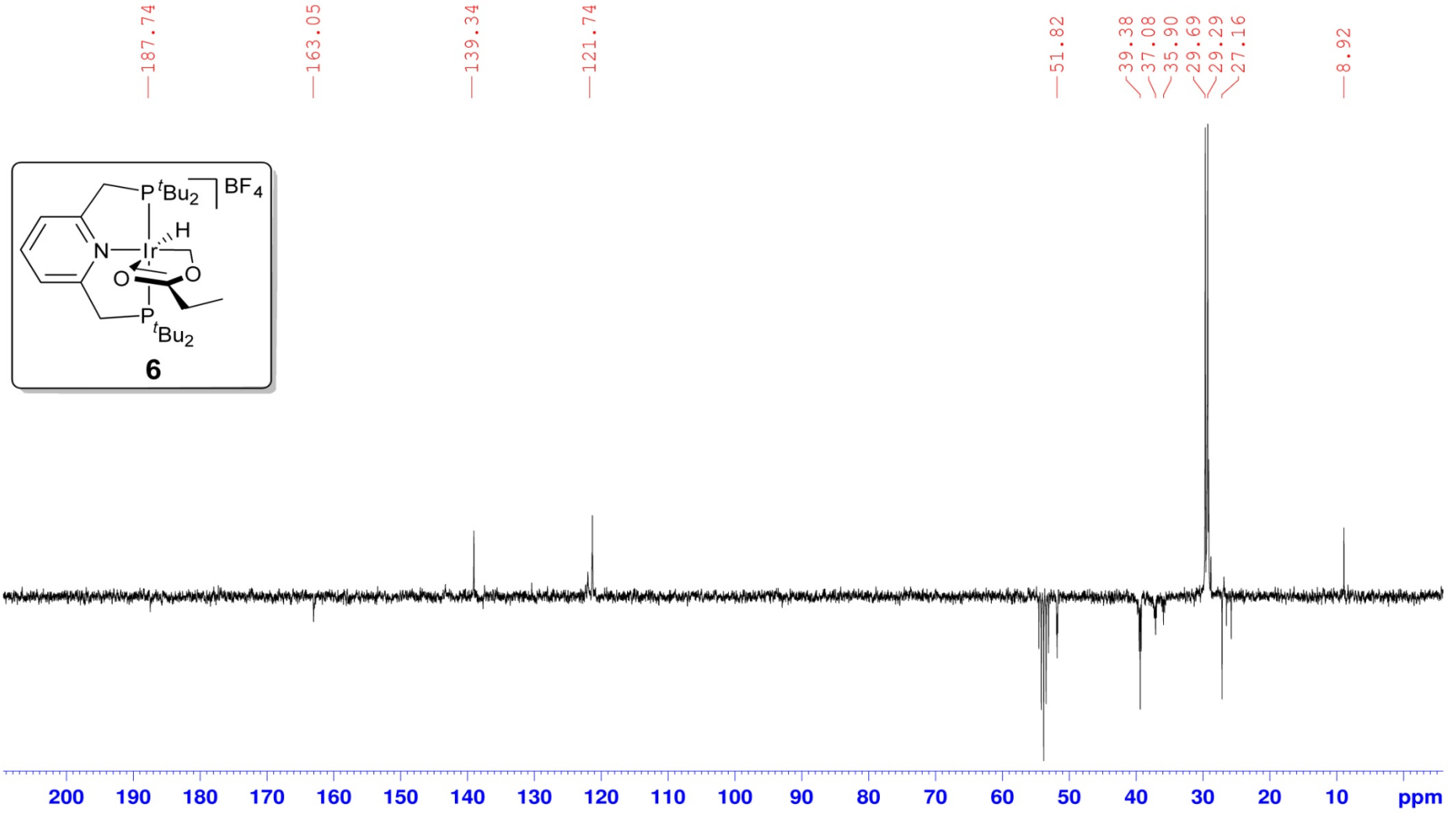
187.74
163.05
139.34
121.74
51.82
39.38
37.08
35.90
29.69
29.29
27.16
8.92
P tBu2
BF4
H
N
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180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

O SECTION S-4: REFERENCES

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